

**PAPER-BASED SENSOR FOR WATER-SOLUBLE  
GASES DETECTION**

**ESTHER CHONG YEE XIN**

**UNIVERSITI TUNKU ABDUL RAHMAN**

**PAPER-BASED SENSOR FOR WATER-SOLUBLE GASES  
DETECTION**

**ESTHER CHONG YEE XIN**


**A project report submitted in partial fulfilment of the  
requirements for the award of Bachelor of Science  
(Honours) Physics**

**Lee Kong Chian Faculty of Engineering and Science  
Universiti Tunku Abdul Rahman**

**May 2023**

## DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

Signature :  \_\_\_\_\_

Name : Esther Chong Yee Xin \_\_\_\_\_

ID No. : 1901960 \_\_\_\_\_

Date : 20/5/2023 \_\_\_\_\_

**APPROVAL FOR SUBMISSION**

I certify that this project report entitled “**PAPER-BASED SENSOR FOR WATER-SOLUBLE GASES DETECTION**” was prepared by **ESTHER CHONG YEE XIN** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Bachelor of Science (Honours) Physics at Universiti Tunku Abdul Rahman.

Approved by,

Signature

:



Supervisor

:

Dr. Tan Chun Hui

Date

:

20/5/2023

## **COPYRIGHT**

The copyright of this report belongs to the author under the terms of the copyright Act 1987 as qualified by Intellectual Property Policy of Universiti Tunku Abdul Rahman. Due acknowledgement shall always be made of the use of any material contained in, or derived from, this report.

© 2023, ESTHER CHONG YEE XIN. All right reserved.

## **ACKNOWLEDGEMENTS**

I would like to thank everyone who contributed to the successful completion of this project. I would like to express my gratitude to my research supervisor, Dr. Tan Chun Hui for his invaluable advice, guidance and his enormous patience throughout the development of the research. In addition, I would also like to express my gratitude to Thiresamary Kurian and Vinod Ganesan who provided me with guidance on experimental setup and data collection.

## ABSTRACT

In this work, an inexpensive and environmentally friendly colorimetric paper-based sensor for rapid detection of water-soluble gases is fabricated. The detection principle is based on colour change upon exposure to water-soluble gases to anthocyanin-containing filter paper, which can be observed by the naked eye. The paper-based sensor is fabricated from red cabbage powder, ethanol, deionized water, filter paper, and different concentrations of polyvinyl alcohol (PVA). The colour change of the sensor is characterised by a UV-Visible Spectrophotometer (UV-Vis), a colorimeter, and an optical microchip sensor (SparkFun MAX30105). The paper-based sensor shows colour changes from reddish-purple to pink upon exposure to acidic gas (pH 0-1) and reddish-purple to green upon exposure to alkaline gas (pH 11–13). The highest total colour change  $\Delta E$ , peak shift, and recovery time are 65.8872, 55 nm, and 4.11 minutes, respectively, exhibited by a paper-based sensor with 20 mg/ml PVA when exposed to 15 ppm alkaline gas. The paper-based sensor also recovered its colour as it is exposed to ambient air. These results indicate that a paper-based sensor that contains 20 mg/ml PVA is a good indicator for water-soluble gases, and it is reusable.

## TABLE OF CONTENTS

<b>DECLARATION</b>		<b>i</b>
<b>APPROVAL FOR SUBMISSION</b>		<b>ii</b>
<b>COPYRIGHT</b>		<b>iii</b>
<b>ACKNOWLEDGEMENTS</b>		<b>iv</b>
<b>ABSTRACT</b>		<b>v</b>
<b>TABLE OF CONTENTS</b>		<b>vi</b>
<b>LIST OF TABLES</b>		<b>viii</b>
<b>LIST OF FIGURES</b>		<b>ix</b>
<b>LIST OF SYMBOLS / ABBREVIATIONS</b>		<b>xi</b>
<b>CHAPTER</b>		
<b>1</b>	<b>INTRODUCTION</b>	<b>1</b>
1.1	General Introduction	1
1.2	Importance of the Study	2
1.3	Problem Statement	2
1.4	Aim and Objectives	3
1.5	Scope and Limitation of the Study	3
1.6	Contribution of the Study	4
1.7	Outline of the Report	4
<b>2</b>	<b>LITERATURE REVIEW</b>	<b>5</b>
2.1	Water-soluble Gas Sensors	5
2.1.1	Paper-based Sensors	5
2.1.2	Electrochemical Sensors	6
2.1.3	Optical Sensors	6
2.1.4	Colorimetric Sensor	8
2.2	Water-soluble Gas	9
<b>3</b>	<b>METHODOLOGY AND WORK PLAN</b>	<b>11</b>
3.1	Introduction	11
3.2	Project Planning	11



3.3	Fabrication of Colorimetric Dye Solution	11
3.3.1	Red Cabbage Dye	12
3.3.2	Polyvinyl alcohol	13
3.4	Fabrication of Colorimetric Paper-based Sensor	14
3.4.1	Filter Paper	15
3.5	Gas Sensing and Characterization of Colorimetric Paper-based Sensor	15
3.5.1	Ultraviolet-Visible Spectroscopy	16
3.5.2	Colorimetric Measurement	18
3.5.3	Hydrochloric acid (HCl)	20
3.5.4	Ammonia (NH <sub>3</sub> )	20
3.6	Integrated Signal with Diffuse Reflective Microchip	21
3.6.1	Optical Microchip Sensor	22
3.6.2	Arduino UNO	24
3.7	Software	25
3.7.1	Arduino IDE	25
<b>4</b>	<b>RESULTS AND DISCUSSION</b>	<b>27</b>
4.1	Optical Absorption Spectra of Colorimetric paper-based sensor	27
4.2	Colour Change and Peak Shift of Colorimetric Paper-based sensor	29
4.3	Integration of Paper-based Sensor Colour Change	32
<b>5</b>	<b>CONCLUSIONS AND RECOMMENDATIONS</b>	<b>36</b>
5.1	Conclusion	36
5.2	Recommendations For Future Work	36
	<b>REFERENCES</b>	<b>38</b>

**LIST OF TABLES**

Table 2.1:	Different Techniques for Optical Gas Sensor (Bogue, 2015).	7
Table 3.1:	Variables of MAX30105 Microchip Sensor.	25
Table 4.1:	Colour Change of Paper-Based Sensor with Different PVA Concentration to HCL Gas and NH <sub>3</sub> Gas.	31
Table 4.2:	Data obtained from transient response upon exposure NH <sub>3</sub> gas.	35
Table 4.3:	Data obtained from transient response during recovery.	35

## LIST OF FIGURES

Figure 2.1:	Food Quality Monitoring Using Colorimetric Dyes and Smart Phone Detection (Chen <i>et al.</i> , 2017).	9
Figure 3.1:	Steps for Fabrication of Colorimetric Dye Solution.	12
Figure 3.2:	Colour Changes for Red Cabbage Extract. (Abedi-Firoozjah <i>et al.</i> , 2022).	13
Figure 3.3:	Molecular Structure of Anthocyanins Changes According to pH (Kan <i>et al.</i> , 2017).	13
Figure 3.4:	Step for Fabrication of Colorimetric Paper-based Sensor.	14
Figure 3.5:	Type of Filter Paper Used.	15
Figure 3.6:	Elements in a Single Beam UV-Vis Spectrometer.	17
Figure 3.7:	Semi-micro cuvette.	17
Figure 3.8:	RGB colour space in coordinate planes.	19
Figure 3.10:	Hydrochloric Acid (Sigma-Aldrich, n.d.).	20
Figure 3.11:	Ammonium Hydroxide (Sigma-Aldrich, n.d.).	21
Figure 3.12:	Setup of The Gas Chamber and Microchip for Real-Time Monitoring.	22
Figure 3.13:	Detection Methods of Optical Reflective Sensors.	23
Figure 3.14:	Optical Microchip Sensor (SparkFun, 2019).	23
Figure 3.15:	Arduino UNO R3 Atmel ATmega328P Compatible.	24
Figure 3.16:	Connection of MAX30105 to Arduino UNO (SparkFun, 2019).	24
Figure 4.1:	Optical Absorption Spectra and Colours of Paper-Based Sensor Exposure To (a) HCl Gas And (b) NH <sub>3</sub> Gas.	28
Figure 4.2:	Colour Shift of Anthocyanin Molecule (Kan <i>et al.</i> , 2017).	29
Figure 4.3:	Total Colour Change and Peak Shift of The Paper-Based Sensor Upon Exposure to (A) HCl Gas and (B) NH <sub>3</sub> Gas.	30
Figure 4.4:	Colour Change of Response and Recovery from Water Soluble Gases.	32

Figure 4.5: Signal Response of Paper-based sensor

34

## LIST OF SYMBOLS / ABBREVIATIONS

$A$	Absorption, AU
$c$	Concentration of The Sample, mol L <sup>-1</sup>
$\Delta E$	Total Colour Change
$I$	Final light intensity, Wm <sup>-2</sup>
$I_0$	Incident Light Intensity, Wm <sup>-2</sup>
$l$	Path Length of Light, cm
$R_0$	Initial Intensity of Paper-Based Sensor
$t_1$	Starting Time of Exposure, minutes
$t_2$	Stopping Time of Exposure, minutes
$\varepsilon$	Molar Absorptivity, L mol <sup>-1</sup> cm <sup>-1</sup>
$\tau_{REC}$	Recovery Time Constant, minutes
$\tau_{RES}$	Response Time Constant, minutes
3D	Three-Dimensional
CH <sub>4</sub>	Methane
CL	Chemiluminescence
Cl <sub>2</sub>	Chlorine
CO	Carbon Monoxide
CRDS	Cavity Ring-Down Spectroscopy
DIAL	Differential Absorption LIDAR
DOAS	Differential Optical Absorption Spectroscopy
FTIR	Fourier Transform Infra-Red
HCl	Concentrated Hydrochloric Acid
I <sup>2</sup> C	Inter-Integrated Circuit
IDE	Integrated Development Environment

IoT	Internet of Things
LED	Light-Emitting Diode
NDIR	Non-Dispersive Infra-Red
NH <sub>3</sub>	Ammonia
NH <sub>4</sub> OH	Ammonium Hydroxide
PAS	Photoacoustic Spectroscopy
PID	Photoionization Detection/Detector
PVA	Polyvinyl Alcohol
RGB	Red, Green, and Blue
SERS	Surface Enhanced Raman Spectroscopy
SpO <sub>2</sub>	Blood Oxygen Saturation Level
TDLAS	Tuneable Diode Laser Absorption Spectroscopy
UVF	UV Fluorescence
UV-Vis	UV-Visible Spectrophotometer

## CHAPTER 1

### INTRODUCTION

#### 1.1 General Introduction

Sensors are currently in high demand, especially following the development of the Internet of Things (IoT), where everything could be sensed and integrated into data, including gas sensors. It was recorded that the first few gas testers or gas detectors were found in the early 19th century. The gas detector was used to detect methane, a colourless, odourless, and flammable gas, by holding a lighted wick and walking around a certain area. However, this process is dangerous, especially to the person who is holding the wick, and an explosion would occur when too much methane is exposed. A type of bird called a canary was also used to detect methane gas in the mining industry since lighted wicks are too dangerous. In the 1920s, a major advancement was made when a catalytic combustion sensor was invented by researchers at the Standard Oil Company to detect combustible gases using a platinum catalyst. As gas sensors developed, the ability to measure one gas and the precise measurement of concentration of gas present was achieved.

These days, electronic gas sensors are much preferred, and they are widely used in industries such as medical, automotive manufacturing, food quality control, and environmental monitoring. Gas sensors play an important role in the medical field because the quality of the air in a hospital needs to be monitored, and they are also used to detect oxygen or carbon dioxide levels in humans. The need for gas sensors is essential in our daily lives because many harmful gases like carbon monoxide (CO), methane (CH<sub>4</sub>), ammonia (NH<sub>3</sub>), and chlorine (Cl<sub>2</sub>) are present in the air (Singh et al., 2018). These gases are water-soluble, which may further pollute soils, streams, rivers, and endangering ecosystems.

Paper-based sensors are an alternative technology that is attractive because it is easy to fabricate, flexible, and low-cost. It is exceptionally helpful in resource limited settings (Singh et al., 2018) and when rapid detection is needed because it is portable and small. Paper-based sensors allow further advancement in microelectronics, biotechnology, microelectronics, and

nanotechnology (López-Marzo & Merkoçi, 2016). This is because it is mainly composed of paper, which has the properties of good passive liquid transport. The use of paper as a substrate for sensing dates back to 1956, when it was used to detect glucose in urine (Liana et al., 2012) and in lateral flow tests. Further advancements in microfluidics are being explored these days, which involve complex three-dimensional (3D) geometries to improve the sensitivity and accuracy of paper-based sensors (Liana et al., 2012).

Red cabbage dye is a natural acid-base indicator that changes colour according to pH value. It changes colour due to anthocyanins that are present in the red cabbage, and the colour changes are distinct enough to be detected by the naked eye. Red cabbage dye is nontoxic, which makes it suitable for wearable devices and also food quality monitoring. Natural dyes are generally biodegradable, meaning they have a lower environmental impact when disposed of.

## **1.2 Importance of the Study**

Through this study, affordable and simple paper-based sensors are fabricated where harmful gases like chlorine, carbon monoxide, and ammonia are detectable. This sensor is applicable in a resource limited setting without any supervision because it is flexible, small, and simple to understand. The colorimetric dye used to fabricate this paper-based sensor is reversible, meaning it can be used repeatedly for a number of times before being disposed of, and since the materials used to fabricate this sensor are biodegradable, it is environmentally friendly and safe to dispose of.

## **1.3 Problem Statement**

Toxic gas monitoring is essential these days, as the air quality is getting worse due to harmful gases released in everyday life by factories, burning fossil fuels, fertilisers, chemical production, and many more. This increases the need for gas sensors, but the ones that are available commercially generally need a power source to function, are expensive, and are bulky because they are mostly produced for industrial purposes, which are not suitable for everyday life.

There are many types of gas sensors, but most of them are mainly composed of metal oxides and conductive polymers. The drawbacks of using



metal oxides are high power consumption and high-temperature operation. These could be overcome by a paper-based sensor because it uses colorimetric sensing, which does not need electricity to operate. Generally, gas sensors have a short lifespan, especially those that are made from conductive polymers. This means that they have to be changed and disposed of frequently, which is not environmentally friendly because conductive polymers and metal oxides are not biodegradable. Whereas for paper-based sensors, it is biodegradable and can be easily disposed of.

There have also been a few studies on fabricating colorimetric sensors for gas detection using acid-base indicators such as methyl red, bromocresol blue, and bromocresol green because of their wide range of colour shift properties, but many of them are toxic, which can cause skin irritation and be harmful when digested. Thus, they are not used in the food industry as they are not safe if consumed and may cause allergic reactions. Since red cabbage dye is extracted from food and safe to consume, it can replace the use of chemical acid-base indicators. Therefore, a paper-based sensor using red cabbage dye is one of the alternative ways because it has the properties that are advantageous for gas detection, and the materials used to fabricate it are inexpensive and easy to obtain.

#### **1.4 Aim and Objectives**

1. To investigate the chemical and optical properties of anthocyanin extract from natural plants as a colorimetric dye for paper-based gas sensors.
2. To understand the effect of the polyvinyl alcohol ink matrix on the optical properties and gas sensing performance of the paper substrate.

#### **1.5 Scope and Limitation of the Study**

This study focuses on fabricating a paper-based sensor for water-soluble gas detection. The substrate used for the sensor is filter paper with red cabbage extract for colorimetric dye. The colour change and optical absorbance of the samples are measured after exposure to water-soluble gases using different measuring instruments at room temperature. This paper-based sensor is further improved by using a diffusely reflective microchip to measure and collect real-time data.

## **1.6 Contribution of the Study**

This study attempts to fabricate a paper-based sensor for water-soluble gas detection that is biodegradable, affordable, and non-toxic, and in doing so, makes an important contribution. First, the air quality of the environment is getting worse as many harmful gases are released each day, which creates an essential need for gas sensors that are simple and small for easy daily use. This study is able to meet the requirement because paper, which is flexible, thin, and small, is used as the substrate for fabricating paper-based sensors, and it is a zero-power sensor. Other than that, food quality, especially the freshness of seafood and meat, is essential to reduce food waste and prevent diseases. This study is able to provide this solution because the paper-based sensor produced allows real-time monitoring for food's freshness and the materials used are food-safe. Other than its contribution to the food industry, this paper-based sensor also meets sustainability requirements. The paper-based sensor fabricated in this study is biodegradable and reusable, which gives an option for reducing waste.

## **1.7 Outline of the Report**

This report consists of the details of the fabrication of a paper-based sensor for water-soluble gas detection and is divided into five chapters. Chapter 1 introduces the background of water-soluble gas sensors, and the aim and objectives are stated clearly in order for project planning. Chapter 2 summarises the reported literature and recent developments on different types of water-soluble gas sensors. Chapter 3 contains the detailed methodology and work plan for this whole project. The materials and instruments used in this work are explained in this chapter. Chapter 4 presents the obtained results used to characterise the paper-based sensor, and the possible reasons for such results are discussed. Chapter 5 concludes the discoveries of the whole project, and recommendations or improvements for future work are discussed.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Water-soluble Gas Sensors

##### 2.1.1 Paper-based Sensors

Recently, paper-based sensors have been drawing much attention, and studies are being made to expand their application because they are easy to fabricate and inexpensive. Most of the advantages of using paper-based sensors are inherited by the characteristics of paper since it is used as a substrate. Sensors that use paper as a substrate are very effective because they have a good absorption for water and gas, which is suitable for detecting water-soluble gas. Paper-based sensors have many types of detection methods because they are able to transfer fluid by capillary action used for microfluidics, separate complex samples by chromatography, and filter (Pinheiro et al., 2021). Paper-based sensors have different ways of fabrication, such as printing, plotting, photolithography, dip-coating, drawing, and cutting (Nery and Kubota, 2013). A paper-based sensor generally uses optical and electrochemical sensing methods due to its characteristics (Nery and Kubota, 2013). Optical detection for paper-based sensors includes colorimetric detection, fluorescence detection, Surface-enhanced Raman spectroscopy (SERS), and transmittance, whereas electrochemical detection includes potentiometric, voltametric, and conductivity-based methods.

Paper-based sensors are proven to be reliable and accurate in their detection abilities. Therefore, they are applied in many important areas, like medical for rapid detection, checking food quality, and environmental inspection. It was mentioned in a journal article by (Kwak et al., 2019) that an ammonia gas sensor that uses paper as a substrate was able to detect ammonia up to 1 ppm at room temperature. There are many studies on paper-based sensors for food safety detection, such as detecting alkaline phosphatase in milk products and detecting growth stimulants in food (Yao et al., 2022). As paper-based sensors are flexible, many modifications can be made to them, such as integration with smartphones or creating a high-density integrated system using components.

### **2.1.2 Electrochemical Sensors**

An electrochemical sensor is a type of sensor that uses chemical properties to detect or measure a specific substance by generating electrical potential from chemical reactions. The chemical reaction in electrochemical sensors happens when they are exposed to targeted water-soluble gases. An electrochemical sensor consists of a transducer and two electrodes, one for reference and another for sensing. There are several types of methods electrochemical sensors use to detect, which are the potentiometric, voltametric, and conductometric methods (Shetti et al., 2019). The potentiometry method measures the potential difference between two electrodes without any current supply. The potential difference was generated by the concentration of hydrogen ions in the electrolyte. The voltametric method works by applying different potentials to electrodes and measuring the resulting current. Lastly, the conductometric method measures the conductivity of the electrolyte when a constant potential is applied to the electrodes.

Generally, electrochemical sensors are inexpensive, have low power consumption, and have a fast response time. However, it has limitations, like needing to be calibrated frequently because it would become insensitive to detecting gases, and environmental factors may affect the results, like temperature change or humidity. In recent studies, researchers have tried to improve the selectivity, reliability, power consumption, and many other aspects of electrochemical sensors. According to (Hanafi et al., 2019), it was mentioned that engineered materials are the key component to improving the capability of an electrochemical sensor, and the sensitivity of ion selection can increase the selectivity. In a study done by (Nie, Nijhuis, et al., 2010) a paper-based electrochemical sensing device was created to detect lead (II) in aqueous solutions for environmental monitoring (Nie, Deiss, et al., 2010).

### **2.1.3 Optical Sensors**

Optical sensing is one of the methods used to detect water-soluble gases and it is widely used in the industry such as healthcare, explosion prevention, food production and many more. This is possible due to most gases absorb light in the spectrum of infrared and ultraviolet. Compared to other types of sensors, the pros of using optical gas sensors are their high sensitivity, selectivity, speed and

ability to withstand high temperature and pressure. The technology of optical sensors has developed rapidly where it is able to detect the amount of gas and the visualisation of gas plumes in real-time (Bogue, 2015). There are several types of optical sensor that uses different principle to detect water-soluble gas such as absorption-based sensors, fluorescence-based sensors, and ionisation-based sensor. There are many techniques a sensor used to detect gases based on each principle (shown in Table 2.1).

Table 2.1: Different Techniques for Optical Gas Sensor (Bogue, 2015).

<b>Principle</b>	<b>Specific Techniques</b>
<b>Absorption</b>	Photoacoustic spectroscopy (PAS) Gas cloud imaging UV absorption Non-dispersive infra-red (NDIR) Differential optical absorption spectroscopy (DOAS) Fourier transform infra-red (FTIR) Cavity ring-down spectroscopy (CRDS) Differential absorption LIDAR (DIAL) Tuneable diode laser absorption spectroscopy (TDLAS)
<b>Luminescence/ fluorescence</b>	Chemiluminescence (CL) UV fluorescence (UVF)
<b>Ionisation</b>	Photoionization detection/detector (PID)

An absorption-based sensor works based on the Beer-Lambert law, where a specific amount of light passes through the gas and is measured. The gas concentration depends on how much light is absorbed by the gas. Fluorescence-based sensors detect the light wavelength emitted by gases. When gas absorbed the incident light at a specific wavelength, it would emit a different wavelength of light. An ionisation-based sensor detects gas by ionising the gas molecules with two electrodes. When the gases pass through between two electrodes, it creates a flow of ions, and the current measure would be interpreted as the concentration of gas. The types of absorption-based sensors are chosen based on the capabilities of the sensor to work in a specific

environment and its requirements. The research for better sensitivity, lower power consumption, and smaller sensors is still going strong because it can be integrated into smart devices, wearables, and smartphones, causing it to be highly in demand (Popa & Udrea, 2019).

#### **2.1.4 Colorimetric Sensor**

Colorimetric sensing methods have been one of the most important sensing techniques because of their wide range of applications. It detects and measures targeted substances through colour change. This method can be used to detect water-soluble gases because the receptor molecule of the colorimetric sensor can bind with targeted molecules (Mauriz, 2020). Colorimetric sensing uses colorimetric dyes such as thymol blue, methyl red, phenol red, and bromophenol blue, which have the property of changing colour due to chemical reactions (Lin *et al.*, 2018). Most colorimetric dyes have a fast response time, changing colour within seconds when exposed to objects. Colorimetric sensing has the advantage of allowing sensors to be battery-free because changes can be seen with the naked eye. However, changes in colour using eye detection are subjective. Therefore, a transducer can be used to measure and detect the changes in colour intensity in numerical data, giving more accurate and highly sensitive colour changes.

Colour information can be represented in the form of red, blue, and green (RGB),  $L^*a^*b^*$ , or  $L^*C^*H$  (Gilchrist & Nobbs, 2017) and each value describes the specific intensity of different colours. Devices like colorimeter are very sensitive to colour changes where it can detect small changes. A colorimetric geometric barcode sensor to examine food quality was successfully fabricated in a study by Chen *et al.* (2017) as it combines the technologies of colorimetric dyes and smartphone detection (shown in Figure 2.1). The use of smartphone for colorimetric detection was also proven to be as accurate as a spectrometer in the research by Shen, Hagen and Papautsky (2012).

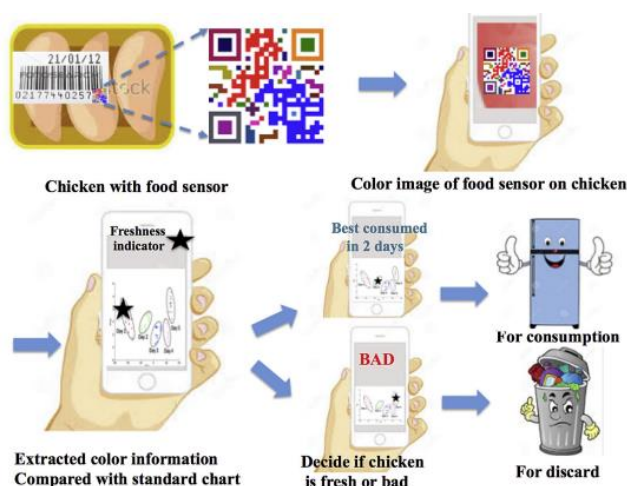


Figure 2.1: Food Quality Monitoring Using Colorimetric Dyes and Smart Phone Detection (Chen et al., 2017).

## 2.2 Water-soluble Gas

Water-soluble gases are gases that are able to dissolve easily in water, forming a solution. The process of forming the solution is called dissolution. This process happens when water-soluble gas is exposed to water, and the gas molecules interact with the water molecules. Some examples of water-soluble gases are oxygen, ammonia, carbon dioxide, chlorine, and many more. All of these gases have different solubility in water, and ammonia has a very high solubility compared to other gases.

Water-soluble gases can be harmful when exposed to humans. When it is in gas form, it will be inhaled by humans, increasing the risk of respiratory diseases. Most of the harmful gases appear to be colourless, and some are odourless, which makes it difficult for humans to detect them by using their senses. When these harmful water-soluble gases dissolve in water, they will form an acidic or alkali solution. For example, sulphur dioxide would dissolve to form sulfuric acid, nitrogen dioxide would dissolve to form nitric acid, and ammonia would dissolve to form aqueous ammonia, which is a basic solution.

Harmful water-soluble gases can be easily found in our daily lives. Ammonia is an alkaline gas that is commonly used in agriculture as fertiliser. The main source of emissions comes from agriculture, which indirectly contributes to greenhouse gas emissions. Ammonia can also be easily found in foods that are spoiled, especially meat and seafood. Nitrogen dioxide is released

during the combustion of fossil fuels such as coal, oil, and fuel used for cars. Sulphur dioxide is released from burning fossil fuels by power plants and industries like paper pulp manufacturing, cement manufacturing, and metal manufacturing. When these gases are exposed to water, especially when it rains, they cause further pollution in rivers, lakes, and oceans. It would also cause acid rain when both sulphur dioxide and nitrogen oxide are present.



## CHAPTER 3

### METHODOLOGY AND WORK PLAN

#### 3.1 Introduction

This chapter focuses on the precise way of conducting this research to achieve the aim and objective which is to fabricate a paper-based sensor for detecting water-soluble gas. A colorimetric matrix is first prepared and coated onto the paper substrate. For detection water-soluble gas, ammonia is used and the colour change, response time, and recovery time will be observed.

#### 3.2 Project Planning

This project aims to fabricate a paper-based sensor for water-soluble gas detection and investigate the chemical and optical properties of anthocyanin from red cabbage extract as a colorimetric dye for a paper-based gas sensor. The materials used for the fabrication of paper-based sensors are gathered, and then the colorimetric dye solution is prepared by mixing the materials. Post baking is done by dipping the filter paper into the colorimetric dye solution. The optical property of the colorimetric dye is obtained using UV-Vis and colorimetry to quantify the colour before and after exposure to water-soluble gas. The colour intensity of the paper-based sensor is collected by attaching it to the SparkFun MAX30105 optical microchip sensor for real-time monitoring. The results obtained are analysed and discussed.

#### 3.3 Fabrication of Colorimetric Dye Solution

The matrix solutions are prepared by first mixing the ethanol and deionized water in a ratio of 1:1. Then 0.1 g/ml of red cabbage powder is dissolved into the mixture of ethanol and deionized water. The solution is heated to 90°C and stirred at 450 rpm using a water bath. After 2 hours of stirring, the mixture is poured into a centrifuge tube and placed into a centrifuge machine (Sigma 3-18k) at 5000 rpm and a temperature of 25°C for 3 minutes. Centrifugation is done to separate the excess insoluble compound, leaving it at the bottom of the centrifuge tube. The solution is filtered using nylon syringe filters with a pore size of 0.45µm (Evergreen) after the centrifugation. The matrix solution is

separated into 6 individual bottles, and different amounts of polyvinyl alcohol (PVA) are added. The amounts of PVA used in this study are 0 mg/ml, 10 mg/ml, 20 mg/ml, 30 mg/ml, 40 mg/ml, and 50 mg/ml. The individual bottles are heated to 135°C and stirred at 450 rpm for 6 hours to dissolve the PVA. The preparation for colorimetric dye solution is illustrated in Figure 3.1.

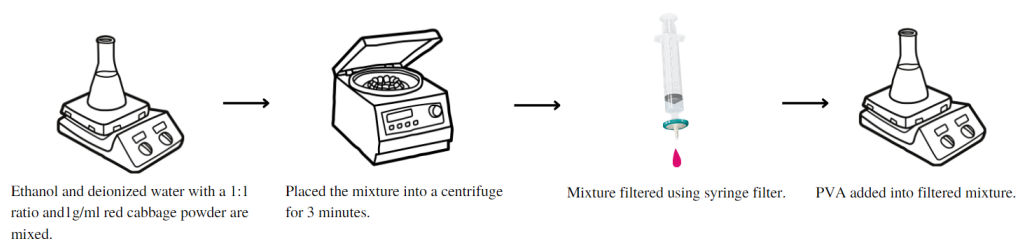


Figure 3.2: Steps for Fabrication of Colorimetric Dye Solution.

### 3.3.1 Red Cabbage Dye

Red cabbage dye is known to be a good natural pH indicator because of its ability to display a wide variety of colours when exposed to different pHs. The compound that gave red cabbage dye this ability is anthocyanins, which are sensitive to pH variations and can also be found in grapes, berries, and eggplants. This makes red cabbage dye a suitable material for fluorescent or colorimetric detection methods that are detectable by the naked eye. The response time for the red cabbage dye to change colour pH is very short, so it is able to detect the changes immediately, and the colour change is very distinctive. Anthocyanins have a natural colour of reddish purple, and they appear the same colour when they are at pH 7. As it is exposed to acidic fluid with a pH less than 7, it will turn pink or red, and it will turn bluish green when exposed to alkaline fluid that is more than pH 7 (shown in Figure 3.2). The change in colour is due to structural changes in the anthocyanins. At low pH, the oxonium ion gives an extended conjugation of the double bond (Chigurupati et al., 2002) in the molecular structure of anthocyanins, making it absorb photons in the blue and green spectrum, causing it to appear red to the naked eye. Whereas in an alkaline solution, the positive charge would be delocalized from the  $\pi$ -electron system (Malins et al., 1999) causing it to absorb photons from the yellow-orange spectrum, giving it a blueish green colour. It was shown that the colour change of the red cabbage dye is reversible along with the change of pH, so the indicator

is able to be reused (Chigurupati et al., 2002). This is possible because the bonds are able to break and form continuously according to the change in pH (shown in Figure 3.3). Red cabbage extract also has the property of being soluble in water, which makes it easy to apply to paper during fabrication. Even though there have been many types of indicators available like chlorophenol red and bromophenol blue, red cabbage dye is a better option because it is nontoxic where it is commonly used as food colour and it is considered a potential natural colour for pharmaceutical use (Chigurupati et al., 2002). This ensures that red cabbage dyes are safe to use as one of the materials for food sensing.



Figure 3.3: Colour Changes for Red Cabbage Extract. (Abedi-Firoozjah et al., 2022).

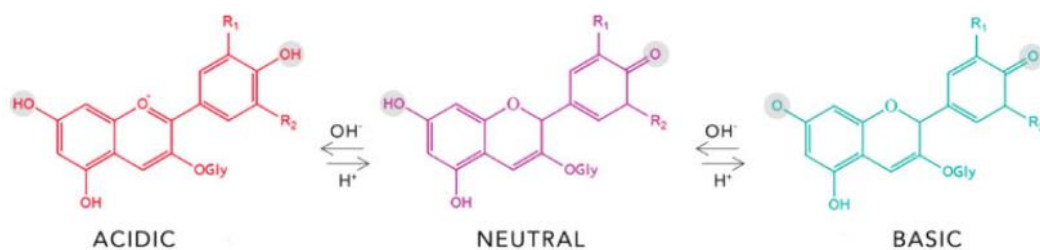


Figure 3.4: Molecular Structure of Anthocyanins Changes According to pH (Kan et al., 2017).

### 3.3.2 Polyvinyl alcohol

Polyvinyl alcohol is one of the materials that are widely used in industries such as making papers, packaging, and eye drops. PVA has been proven to be non-toxic and relatively harmless; therefore, it is safe to use in industry, especially in the food and medical fields. It is a synthetic polymer with the qualities of being odourless and colourless, and it could be obtained in powder form. It is mainly used to bind or seal things because of its abundant hydroxyl group. It can be added to dye solutions as a pigment binder to enhance the mechanical strength between the colorimetric dye solution and the filter paper without affecting the ability to detect changes in pH (Nisha, 2020). It is also able to

reduce swelling and water solubility of the paper-based sensor (Kuswandi et al., 2020). The hydroxyl group in PVA allows it to form hydrogen bonds with water, making it very soluble in water. However, the solubility of the PVA depends on its concentration and degree of hydrolysis (Harpaz et al., 2019). The higher the degree of hydrolysis, the lower the solubility because the availability of hydrogen to form hydrogen bonds decreases while it interacts within the PVA molecules themselves. Not only that, the solubility of the PVA also depends on the solvent; it is insoluble in organic solvents but highly soluble in water, while it is partially soluble in ethanol (Brough et al., 2016). The concentration of the ethanol also has an effect on the solubility of the PVA, where a lower concentration of ethanol has a higher solubility of PVA due to the water content present in ethanol. PVA has a melting point within the range of 185°C to 225 °C, but it also widely depends on the degree of hydrolysis and concentration (Jamil et al., 2018). The higher the degree of hydrolysis, the higher the melting point of the PVA because more heat is needed to break the hydrogen bond between PVA molecules. However, overheating the PVA-containing solution would form a thick film on the surface of the solution. Generally, PVA is graded by its degree of hydrolysis and viscosity.

### 3.4 Fabrication of Colorimetric Paper-based Sensor

A few filter papers are cut into pieces with an area of 2.5cm x 2.5 cm. The filter papers are then dipped into dye solutions with different concentrations of PVA for 1 minute. The process is followed by the post-baking of the filter paper at 80°C for 1 minute. The preparation for colorimetric paper-based sensor is illustrated in Figure 3.4.

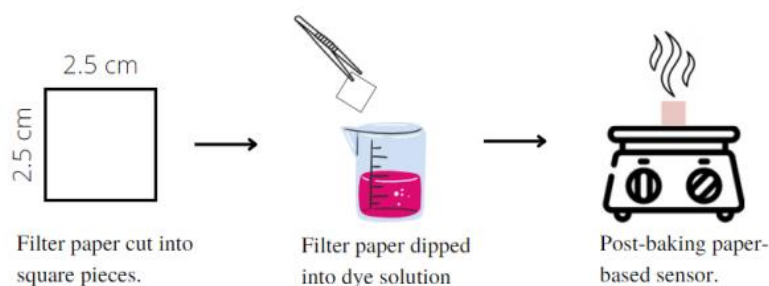


Figure 3.5: Steps for Fabrication of Colorimetric Paper-based Sensor.

### 3.4.1 Filter Paper

There are many types of paper, and the most common type to be used for fabricating paper-based sensors is qualitative filter paper (as shown in Figure 3.6). Filter paper is generally flexible, inexpensive, recyclable, and lightweight, and it has the properties needed to fabricate a sensor. Since filter paper is white, it is suitable to use as a substrate in colorimetric analysis, where the changes in colour are able to be observed with the naked eye. Filter papers are generally semi-permeable papers that are made from cotton fibres, which are the purest form of cellulose (Hsieh, 2007). Cellulose is one of the key components of filter paper because it gives it its wicking ability. Wicking ability allows liquids to flow through the paper due to capillary pressure (Patari and Mahapatra, 2020). Not only that, but cellulose is also a good absorber because it has hydroxy groups between its cell walls ready to interact with water, forming hydrogen bonds with water, making it hydrophilic (Sahu and Gupta, 2022). There are also different properties of filter paper, where parameters like flow rate, weight, thickness, retention, and porosity are different for each type of filter paper.



Figure 3.7: Type of Filter Paper Used.

### 3.5 Gas Sensing and Characterization of Colorimetric Paper-based Sensor

The excess matrix solutions with different PVA are poured into two sets of 6 cuvettes, and they are used to obtain optical absorption between the wavelengths of 350 nm and 750 nm before and after exposure to water-soluble gases by using an ultraviolet-visible (UV-Vis) spectrometer (Agent Cary 300). A 1:1 ethanol and deionized water mixture is used as a reference sample in the UV-Vis. The

intensity of the red, green, and blue (RGB) values for the colorimetric paper-based sensor before and after exposure to water-soluble gases is measured by using a colorimeter (LScolor). Two sets of 6 cuvettes and 7 paper-based sensors that contain different concentrations of PVA are prepared by placing them into two beakers. 100 $\mu$ l of concentrated hydrochloric acid (HCl) and 100 $\mu$ l of ammonium hydroxide (NH<sub>4</sub>OH) are exposed to samples in each beaker for 1 hour, respectively.

### 3.5.1 Ultraviolet-Visible Spectroscopy

Ultraviolet-visible (UV-Vis) spectroscopy is a method used to measure the light absorbed by a sample as a function of wavelength within the UV and visible light spectrums. The range of wavelengths used in this study is 750nm to 350nm. This range was used because the colour change of the paper-based sensor falls within the visible range, and the shift of the peak absorbance wavelength is clearly shown in the graph of absorbance. With these data, information like the chemical composition of a sample can be determined.

UV-Vis works by emitting electromagnetic radiation that carries energy. The amount of energy is inversely proportional to the wavelength of the electromagnetic radiation. The higher the energy of electromagnetic radiation, the shorter the wavelength. When the electromagnetic radiation hits the sample, the electrons of the sample will be excited to a higher level. The specific wavelength of electromagnetic radiation absorbed by a sample corresponds to the amount of energy required to excite the electrons.

A UV-Vis spectrophotometer consists of a light source, a monochromator, a sample, and a detector. Halogen, tungsten, and deuterium light sources are used in the spectrophotometer, where halogen or tungsten lamps are used to emit visible light and deuterium emits UV light. The light source will pass through a monochromator that separates light into specific wavelengths which is illustrated in Figure 3.8. Monochromators work by using gratings that will diffract the light to a specific angle, producing a specific wavelength of light at the groove frequency of the gratings. Groove frequency is the distance between adjacent grooves, which would affect the optical resolution and wavelength range. A higher groove frequency would give better optical resolution; however, it limits the wavelength range because the order of

diffraction becomes lower. Light would pass through a series of filters to remove unwanted wavelengths of light.

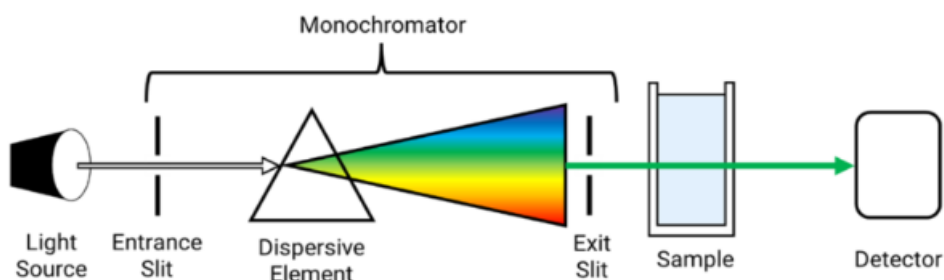


Figure 3.9: Elements in a Single Beam UV-Vis Spectrometer.

For sample analysis, a solvent is used as a reference sample (blank sample) to compensate for the solvent's absorption value. A cuvette is a small vessel used for holding samples in UV-Vis. A cuvette comes in different volumes and materials, but normally a cuvette is able to hold up to 1.5 ml of sample, and the light path that the window of the cuvette provides is 1 cm. Different materials in the cuvette have different transmission ranges of wavelength, which would affect the absorption measurement. For example, a plastic cuvette has a transmission range of 380nm to 850nm, whereas UV quartz allows light to transmit from 220nm to 2500nm. The type of cuvette used in this study is semi-micro cuvette as shown in Figure 3.10.



Figure 3.11: Semi-micro cuvette.

Lastly, the light passed through the sample will hit on a detector which converts light into signals. Detectors use photomultiplier tube (PMT) or

semiconductor that are sensitive to UV and visible light. The signal generated by detector is proportional to the amount of light absorbed by the sample. The absorption of the sample is related to light measured after passing through the sample ( $I$ ) and incident light intensity ( $I_0$ ) shown in Equation 3.1. The relationship between absorption ( $A$ ) and concentration of the sample can be described by Beer-Lambert law according to the following equation:

$$A = \varepsilon cl = \log_{10} \frac{I_0}{I} \quad (3.1)$$

where  $\varepsilon$  is the molar absorptivity of the sample ( $\text{L mol}^{-1} \text{cm}^{-1}$ ),  $c$  is the concentration of the sample ( $\text{mol L}^{-1}$ ) and  $l$  is path length of light through the sample (cm).

### 3.5.2 Colorimetric Measurement

Colorimeter is a device used to measure and determine a colour in the visible light spectrum. It is widely used in the furniture industry, coating industry, plastics, and other fields. The colorimeter used in this study is Linshang LS171 d/8 colorimeter. It has 7 colour space including CIE lab, Luv, LCh, Yxy, CMYK, RGB, and Hex. It also has a colour comparison function using up to 6 different formulas.

Red, green, and blue (RGB) is a system used to represent colours in digital devices such as computers, phones, televisions, and others. This colour model is an additive system where different amounts of primary colour of red, green, and blue are added together to create a wide range of colours (Zelazko, 2022). Each colour is represented in a set of three integer numbers where each number are the intensity of red, green, and blue. The value of intensity for each number are from 0 to 255, where combination of three zeros gives the darkest colour and a set of 255 gives white colour. The RGB value can be presented in coordinate planes as shown in Figure 3.12.



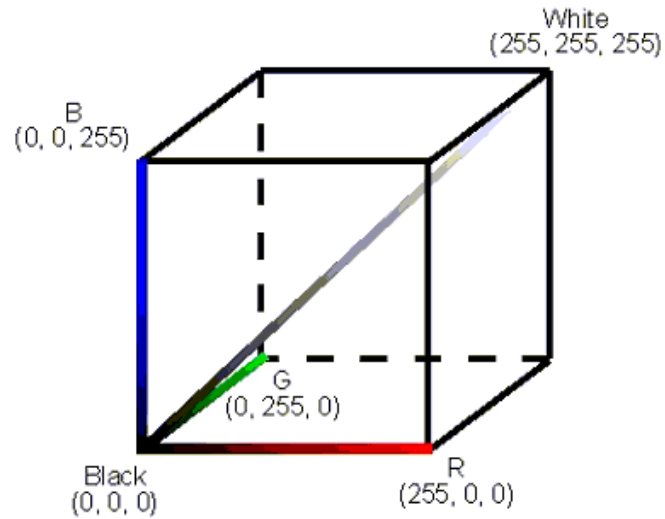


Figure 3.13: RGB colour space in coordinate planes.

In the RGB colour space, the difference between two colours can be measured by using the formula of Euclidean colour distance. The colour distance in RGB colour space can be calculated using the following equation:

$$\Delta E = \sqrt{(R_2 - R_1)^2 + (G_2 - G_1)^2 + (B_2 - B_1)^2}, \quad (3.2)$$

where

$\Delta E$  = total colour change,

$R_2$  = intensity of red after colour change,

$R_1$  = intensity of red before colour change,

$G_2$  = intensity of green after colour change,

$G_1$  = intensity of green before colour change,

$B_2$  = intensity of blue after colour change,

$B_1$  = intensity of blue before colour change.

The value of total colour change obtained from equation 2 represents how far apart two colours are in the RGB colour space. In this study, the colour change of the paper-based sensor is essential to comparing the effect of the concentration of PVA.

### 3.5.3 Hydrochloric acid (HCl)

Hydrochloric acid is a colourless liquid that has a pungent odour. It is highly corrosive, and it is a strong acid composed of hydrogen atoms and chlorine atoms. The pH value of hydrochloric acid ranges from 0 to 1. Hydrochloric acid is a product of hydrogen chloride gas and water, which makes hydrogen chloride a water-soluble gas. It is widely used in laboratories and industries like oil and gas production, water treatment, metal processing, and others. Even though it is commonly used, it is very dangerous when it is not carefully handled, especially when it comes into contact with skin or when inhaled. Some precautions should be taken while handling hydrochloric acid, like using it in a fume hood and wearing proper personal protective equipment. Hydrochloric acid is commonly found with a concentration of 37% and is called concentrated hydrochloric acid (as shown in Figure 3.14). In this study, both concentrated and diluted hydrochloric acid are used for data collection. It is used to observe the response of a paper-based sensor to an acidic, water-soluble gas.



Figure 3.15: Hydrochloric Acid (Sigma-Aldrich, n.d.).

### 3.5.4 Ammonia (NH<sub>3</sub>)

Ammonia is a water-soluble gas, and it readily reacts with water to form ammonium hydroxide (NH<sub>4</sub>OH). Both gaseous and aqueous forms are colourless with a pungent smell. Ammonia is composed of nitrogen atoms and hydrogen atoms that are held together by covalent bonds. It is alkaline, with a

pH value ranging from 11 to 13. Ammonia is toxic and corrosive, making it dangerous when not properly handled. Ammonia should be handled with proper personal protective equipment and in a ventilated area. Despite being dangerous, ammonia is widely used in cleaning agents, fertilisers, plastics, and others. Ammonia hydroxide solution with 28% to 30% concentration (shown in Figure 3.16) is used to release alkaline gas, water-soluble gas in this study to observe the response of a paper-based sensor.



Figure 3.17: Ammonium Hydroxide (Sigma-Aldrich, n.d.).

### 3.6 Integrated Signal with Diffuse Reflective Microchip

For further analysis, the paper-based sensor is attached to an optical microchip sensor (SparkFun, MAX30105) in the gas chamber to obtain a real-time signal on the colour change (illustrated Figure 3.18). Two sets of 6 paper-based sensors with different PVA concentrations are prepared, where 1 set is exposed to ammonia and the other to hydrochloric acid. The paper-based sensor is placed directly above the optical window of the microchip sensor to obtain more accurate results as it affects the intensity. The microchip and paper-based sensor are placed in a gas chamber and connected to a microcontroller (Arduino, UNO R3) that programmes them to emit red and green light and collect the intensity of the respective light. The initial colour intensity of the paper-based sensor was collected for 5 minutes. Then, 100 $\mu$ l of NH<sub>3</sub> gas and HCl gas are exposed,

respectively, in the gas chamber for 10 minutes by dripping it onto a filter paper. The pump of the gas chamber is turned on for 30 minutes to obtain the intensity of the paper-based sensor for recovery.

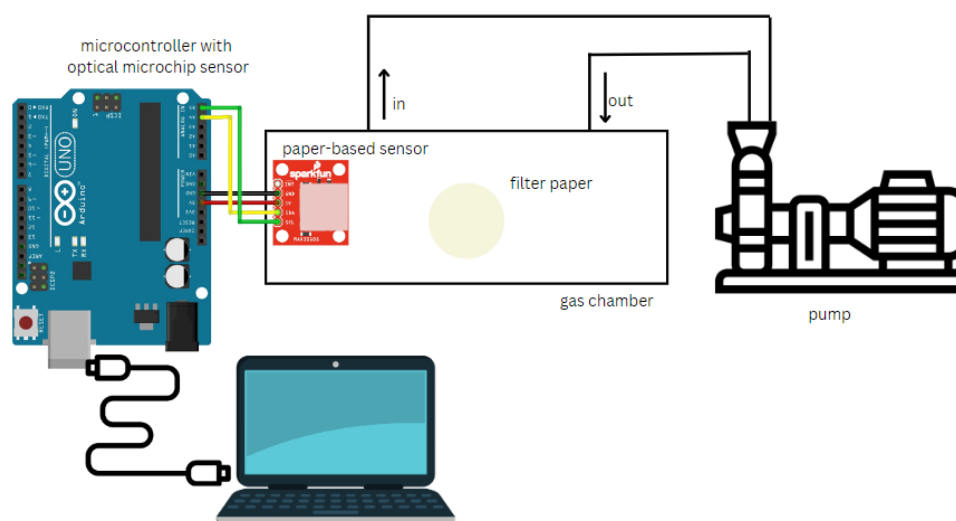


Figure 3.19: Setup of The Gas Chamber and Microchip for Real-Time Monitoring.

### 3.6.1 Optical Microchip Sensor

Other than a colorimeter and UV-Vis, an optical microchip sensor is also able to measure colour intensity. An optical microchip sensor is compact and cheaper than other instruments used for obtaining colour intensity. Optical microchip sensors can be easily found these days in smartwatches and phones to detect pulse and blood oxygen saturation level ( $SpO_2$ ), but there have not been many applications for detecting gases and particles (Deng et al., 2016).

An optical microchip sensor consists of two parts: the transmitter and the receiver. A light-emitting diode (LED) is used as a transmitter and a photodetector as a receiver. It works by first emitting light from the LED, reflecting it off the object, and then receiving the reflected light by the photodetector (shown in Figure 3.20). Different types of LED light that emit different wavelengths from 210 to 1550 nm are available commercially (Yeh et al., 2017), and they can be used in an optically reflective sensor depending on the colour absorption by the target. For example, infrared light would be used in an oximeter because it would be absorbed by the red blood (Doshi &

Panditrao, n.d.). The higher the concentration of the haemoglobin, the redder the blood and more infrared light would be absorbed, changing the waveform reflected back to the photodetector.

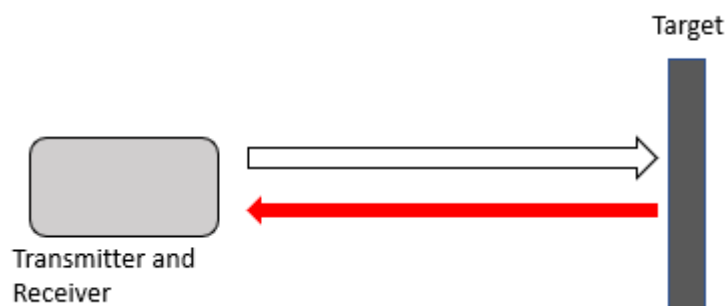


Figure 3.21: Detection Methods of Optical Reflective Sensors.

The colour intensity can also be measured by an optical microchip sensor. SparkFun MAX30105 Particle Sensor (shown in Figure 3.22) is a type of optical microchip sensor that can be used to measure colour intensity. It consists of a red LED, a green LED, and an infrared LED, where the peak wavelength for the red LED is 660 nm, the green LED is 537nm, and the infrared LED is 880nm. These LED sources emit specific wavelengths of light that would be absorbed by the paper-based sensor according to the colour, and the remaining light would be reflected back to the colour sensor. The MAX30105 is operated with a 5V power supply, and it communicates through a microcontroller that supports Inter-Integrated Circuit (I<sup>2</sup>C). The specific function of this sensor is to be programmed into the microcontroller for data collection and display.



Figure 3.23: Optical Microchip Sensor (SparkFun, 2019).

### 3.6.2 Arduino UNO

Arduino UNO as shown in Figure 3.24, is a type of microcontroller board that is used to control devices or systems. This microcontroller board is based on the ATmega328P, and it has 14 digital pins and 6 analogue inputs. Arduino UNO supports communication protocols like I<sup>2</sup>C and SPI that allow it to connect with devices like sensors, electric components, and motors. This microcontroller can be powered by a computer through a power jack with 5 Volts. In this study, the Arduino board was directly connected to the MAX30105 Particle Sensor via jumper wires. The setup of the Arduino board and MAX30105 is shown in Figure 3.15. Arduino IDE is software used to programme Arduino boards, and the programming languages used in Arduino IDE are C++ and C.

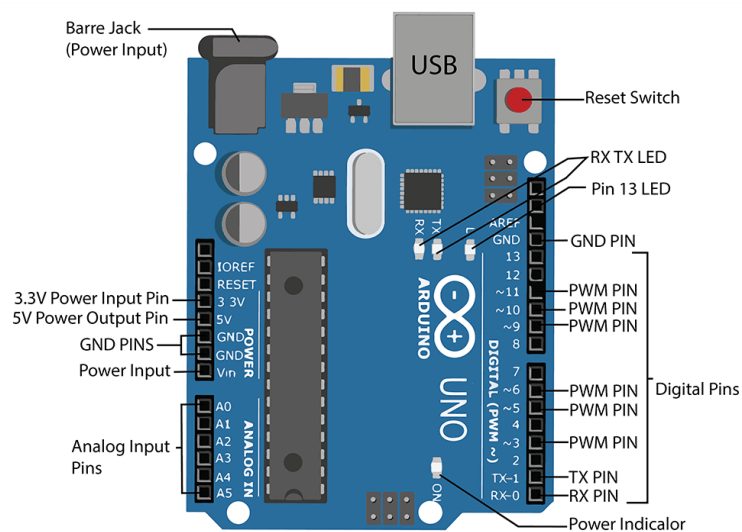


Figure 3.25: Arduino UNO R3 Atmel ATmega328P Compatible.

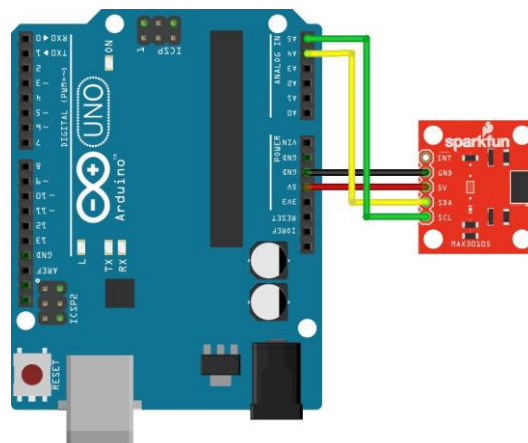


Figure 3.26: Connection of MAX30105 to Arduino UNO (SparkFun, 2019).

### 3.7 Software

There are two pieces of software used in this study, which are Arduino IDE and Origin 2023. The Arduino IDE is used to programme the microcontroller and hardware for data collection. Origin 2023 is used to organise and evaluate the data collected from FTIR, UV-Vis, and optical microchip sensors.

#### 3.7.1 Arduino IDE

Arduino Integrated Development Environment (IDE) is a software used to program Arduino boards. It has a function of writing, compiling and uploading the codes to the Arduino boards and giving specific commands to the hardware. Arduino IDE also receives real-time data from hardware and displaying it on the serial monitor. The programming language Arduino uses is C and C++. In this study, the setup variable of the microchip is shown in Table 3.1.

Table 3.1: Variables of MAX30105 Microchip Sensor.

Specification	Values
LED Drivers	Red + Green + IR
Sample Average per FIFO	8
Sample Rate	200ms
Pulse Width	69 $\mu$ s

The coding algorithm for setting up the MAX30105 Particle Sensor to detect intensity of colour can be found in an open-source library, and it is shown below:

```
#include <Wire.h>
#include "MAX30105.h"
MAX30105 particleSensor;
#define debug Serial
void setup()
{
  debug.begin(9600);
  debug.println("MAX30105 Basic Readings Example");
```

```

// Initialize sensor
if (particleSensor.begin() == false)
{
debug.println("MAX30105 was not found. Please check wiring/power. ");
while (1);
}
byte ledBrightness = 5; //Options: 0=Off to 255=50mA
byte sampleAverage = 8; //Options: 1, 2, 4, 8, 16, 32
byte ledMode = 3; //Options: 1=Red only, 2=Red + IR, 3=Red + IR + Green
byte sampleRate = 200; //Options: 50ms,100ms,200ms,400ms,
                        800ms,1000ms,1600ms, 3200 ms
int pulseWidth = 69; //: 69, 118, 215, 411
int adcRange = 32768; //Options: 2048, 4096, 8192, 16384, ...
particleSensor.setup(ledBrightness, sampleAverage, ledMode, sampleRate,
pulseWidth, adcRange);
}
void loop()
{
debug.print("R-");
debug.print(particleSensor.getRed());
debug.print("G-");
debug.print(particleSensor.getGreen());
debug.println();
}

```

MAX30105 Particle Sensor has 3 LED which are red, green, and infrared. The sensor only allows 3 combination of LED drivers to work at a time: (i) red only, (ii) red and infrared, (iii) red, green and infrared. The width of each pulse emits from LED also can be program range from 69  $\mu$ s to 411  $\mu$ s to optimize the accuracy of colour detection and also power consumption. The sample rate for this microchip was set to 8 sample within 200ms, where 40 data are collected every second.

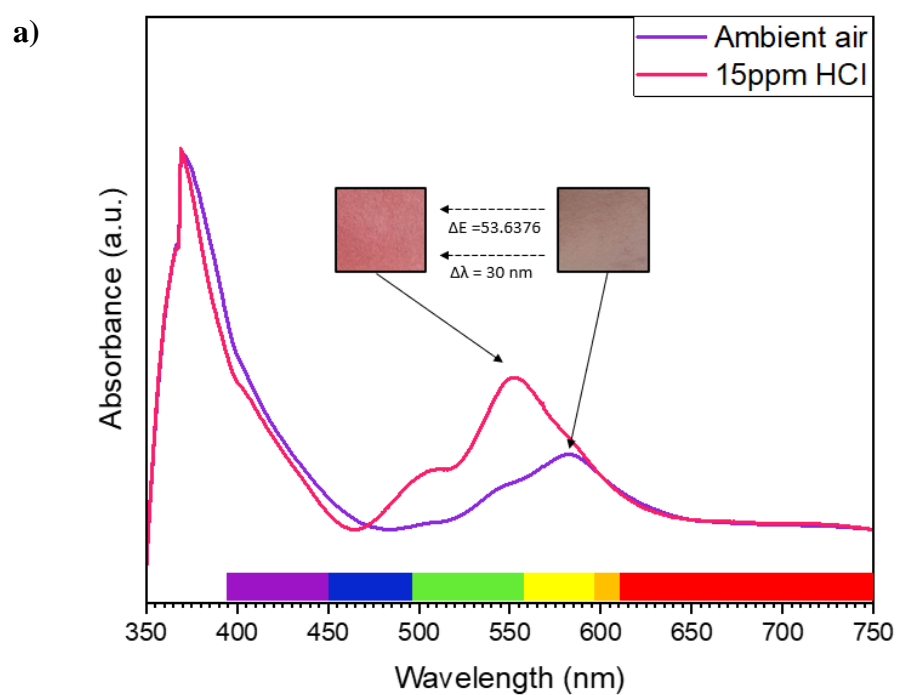


## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Optical Absorption Spectra of Colorimetric paper-based sensor

In this study, colorimetric dye solutions are used to obtain the absorption peak shift, and paper-based sensors are used to obtain the total colour change. The colour changes of the paper-based sensor are characterised using a colorimeter through the absorption method, and a UV-Vis spectrometer is used to obtain the optical absorption spectra. The results are shown in Figures 4.1 (a) and 4.1 (b).



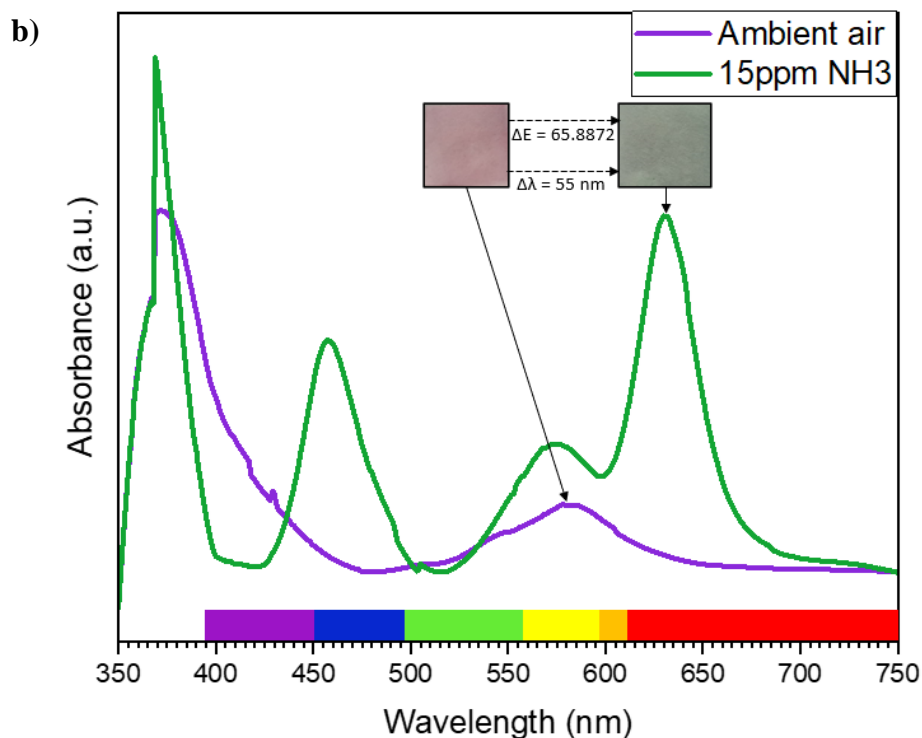


Figure 4.1: Optical Absorption Spectra and Colours of Paper-Based Sensor Exposure To (a) HCl Gas And (b) NH<sub>3</sub> Gas.

As shown in Figures 4.1(a) and 4.1(b), the colorimetric dye solution exhibited an absorption peak shift when exposed to 15 ppm NH<sub>3</sub> gas and 15 ppm HCl gas, respectively. The absorption peak of the colorimetric dye solution shifted from the yellow region to the green region upon exposure to 15 ppm HCl gas. The paper-based sensor absorbs green and yellow regions, giving the appearance of pink after exposure to HCl gas. The absorption peak of the colorimetric dye solution exposed to 15 ppm NH<sub>3</sub> gas shifted from the yellow region to the red region. The initial colour of the colorimetric dye solution is reddish-purple, where yellow light would be absorbed, transmitting purple light at neutral pH. After exposing it to 15 ppm NH<sub>3</sub> gas, the absorption peak is in the red region, transmitting green light.

The reason behind the colour changes and absorption spectra of colorimetric dye solutions and paper-based sensors can be explained through the molecular structure of anthocyanin, a component found in red cabbage dye. The colour changes for both colorimetric dye solutions and paper-based sensors are from a reddish-purple colour to a green colour when exposed to NH<sub>3</sub> gas. This is caused by the protons of anthocyanin molecules being removed from the

phenol groups. Deprotonated anthocyanin molecules would absorb light in the yellow spectrum, giving green appearance. As the colorimetric dye solution and paper-based sensor are exposed to HCl gas, the anthocyanin molecule is protonated, forming a positive ion and giving it a pink appearance. The colour shift of the anthocyanin molecule is illustrated in Figure 4.3 (Kan et al., 2017).

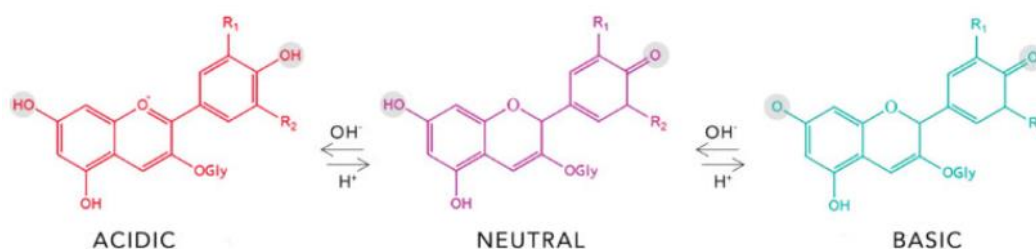


Figure 4.2: Colour Shift of Anthocyanin Molecule (Kan et al., 2017).

#### 4.2 Colour Change and Peak Shift of Colorimetric Paper-Based Sensor

The total colour changes and peak shift of both colorimetric dye solutions and paper-based sensors with concentrations of 0 mg/ml to 50 mg/ml PVA exposed to 15 ppm HCl gas and 15 ppm  $\text{NH}_3$  gas, respectively, are presented in Figures 4.3(a) and 4.3(b). The total colour change of a colorimetric dye solution with 30 mg/ml of PVA is the highest ( $\Delta E = 59.034$ ), but the peak shift is 0 nm. The absorption peak shift before and after exposure to 15 ppm HCl gas is 0nm when the concentration of PVA is 30 mg/ml and above. This is because the solubility of HCl gas decreases when colorimetric dye solutions contain higher concentrations of PVA. The concentration of PVA in colorimetric dye solution is affected by the presence of -OH (hydroxyl group), causing the water uptake to increase or decrease (Jain et al., 2017). In addition, the solubility of HCl gas is lower than that of  $\text{NH}_3$  gas at the same temperature and pressure conditions. This is due to the fact that the intermolecular forces between HCl gas and water molecules are weaker compared to  $\text{NH}_3$  gas. Unlike exposure to HCl gas, there is a peak shift when a colorimetric dye solution with a concentration of PVA of 30 mg/ml and above is exposed to  $\text{NH}_3$  gas, as illustrated in Figure 4.3(b).

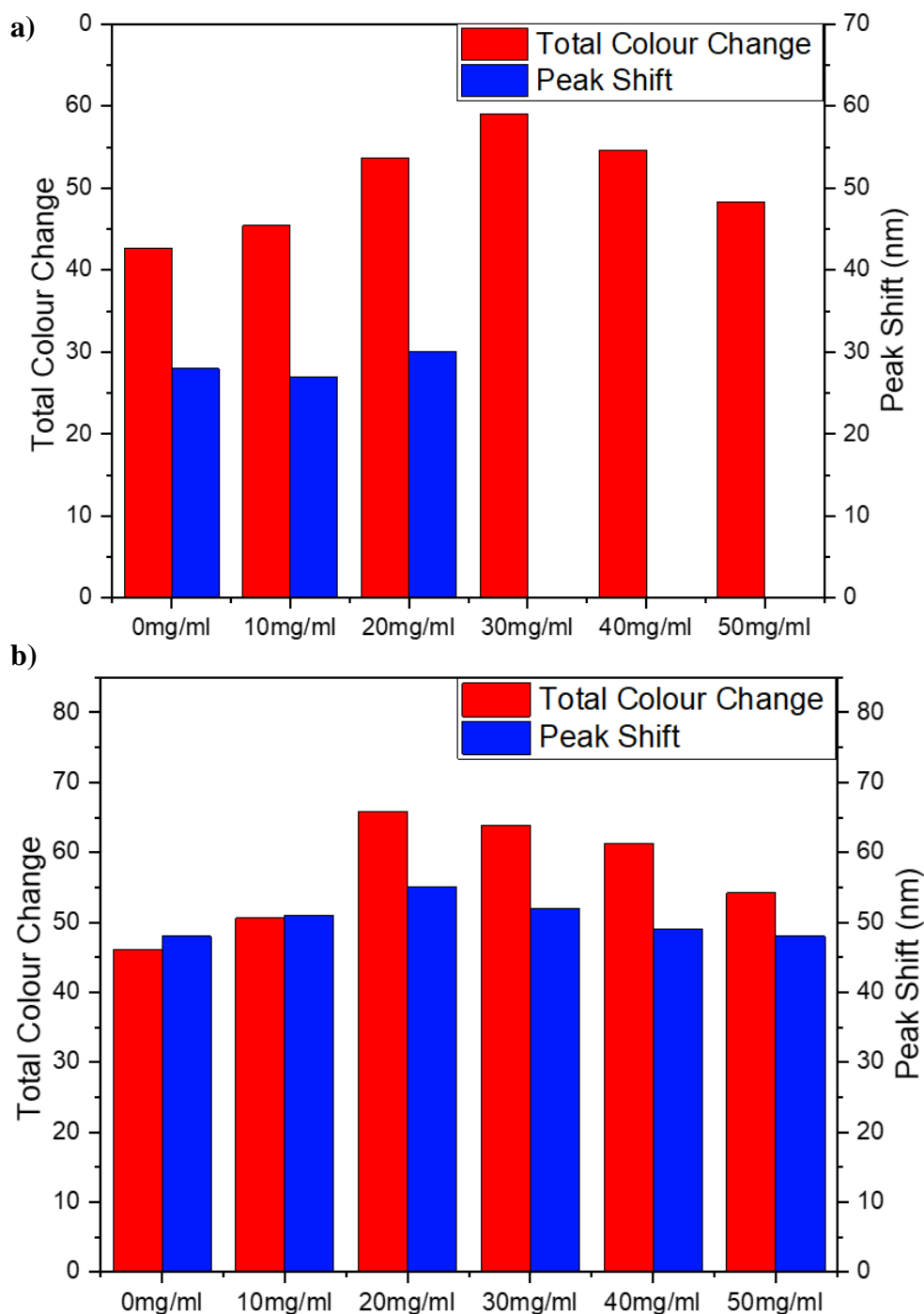
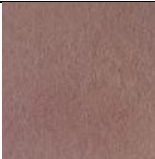

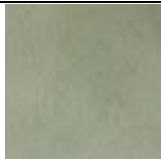
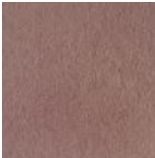

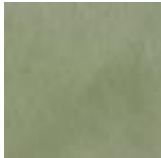

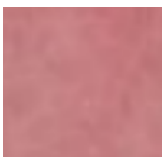

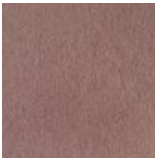


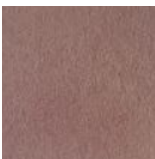
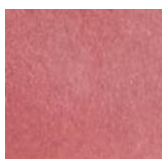

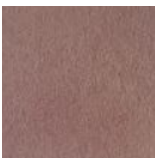
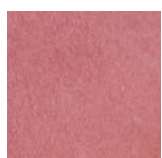



Figure 4.3: Total Colour Change and Peak Shift of The Paper-Based Sensor Upon Exposure to (A) HCl Gas and (B) NH<sub>3</sub> Gas.

The colour changes of paper-based sensors exposed to NH<sub>3</sub> gas and HCl gas are captured and presented in Table 4.1. The colour change upon exposure to acidic and alkaline water-soluble gases can be clearly observed with the naked eye, where reddish purple would change to green and pink, respectively. By comparing the results in Figures 4.3(a) and 4.3(b) with Table

2, the colour intensity of paper-based sensors is related to the total colour change calculated using RGB values. The total colour change for 30 mg/ml of PVA is the highest, and the pink colour intensity is the highest compared to other concentrations when it is exposed to 15 ppm HCl gas. When paper-based sensors with different concentrations of PVA are exposed to NH<sub>3</sub> gas, 20 mg/ml has the highest total colour change, and the intensity of the green colour is strong.

Table 4.1: Colour Change of Paper-Based Sensor with Different PVA Concentration to HCL Gas and NH<sub>3</sub> Gas.

<b>PVA Concentration</b>	<b>Initial colour</b>	<b>Colour after 15ppm HCl</b>	<b>Colour after 15ppm NH<sub>3</sub></b>
<b>0mg/ml</b>			
<b>10mg/ml</b>			
<b>20mg/ml</b>			
<b>30mg/ml</b>			
<b>40mg/ml</b>			
<b>50mg/ml</b>			

The red channel signals are collected during the release of 15 ppm  $\text{NH}_3$  gas and 15 ppm  $\text{HCl}$  gas in the gas chamber, respectively, for 10 minutes. The paper-based sensors are left to recover their colour while being exposed to ambient air. The colour transition of a paper-based sensor upon exposure to water soluble gas and the colour recovery are illustrated in Figure 4.5. The colour changes for exposure to 15 ppm  $\text{HCl}$  gas are reddish-purple to pink. However, when paper-based sensors were set to recover, it did not return to its reddish-purple colour; instead, it stayed pink. This is because the bond that formed between anthocyanins and  $\text{HCl}$  gas is strong, and exposing it to ambient air is not strong enough to break the bond. When paper-based sensors are exposed to 15 ppm  $\text{NH}_3$  gas, they turn green from reddish purple, and they recover back to reddish purple.



Figure 4.4: Colour Change of Response and Recovery from Water Soluble Gases.

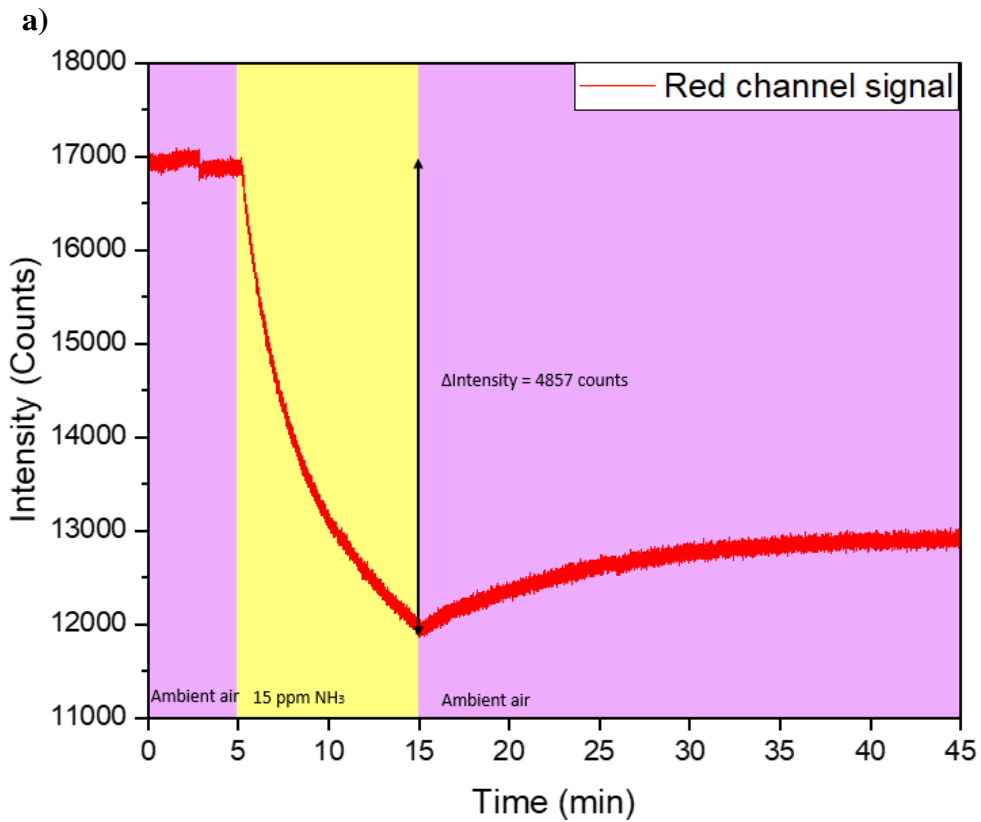
### 4.3 Integration of Paper-based Sensor Colour Change

The paper-based sensor is attached to the MAX30105 microchip, and the red channel signal is recorded to monitor the colour change of the paper-based sensor under ambient air to 15 ppm  $\text{NH}_3$  gas, then back to ambient air (shown in Figure 4.6). The intensity measured by the microchip shows that as the paper-based sensor was exposed to  $\text{NH}_3$  gas, the intensity dropped significantly. This could also be interpreted as the paper-based sensor turning green very fast. As  $\text{NH}_3$  gas is pumped out of the gas chamber, the intensity slowly increases, and the colour slowly changes back to reddish purple.

The transient response of the microchip was used to evaluate the response and recovery time of a paper-based sensor. The signal responses are fitted to a first-order exponential function as given below:

$$R(t) = \begin{cases} R_o \exp\left(-\frac{t}{\tau_{RES}}\right), & t_1 \leq t \leq t_2 ; \\ R_o \left[ \exp\left(-\frac{t}{\tau_{RES}}\right) \times \exp\left(-\frac{t-t_2}{\tau_{REC}}\right) \right], & t \geq t_2. \end{cases} \quad (4.1)$$

where  $R_o$  is the initial intensity of paper-based sensor in ambient air,  $\tau_{RES}$  and  $\tau_{REC}$  represents the time constant for the respective response and recovery phases,  $t_1$  is the starting time of exposure to  $\text{NH}_3$  gas, and  $t_2$  is the stopping time of exposure to  $\text{NH}_3$  gas. The time spent by the microchip to achieve 63.2% of the total intensity change is also represented by  $\tau_{RES}$  and  $\tau_{REC}$ . The fall range and fall time from Figure 4.5 (b) refer to 63.2% of the total intensity dropped and the time spent to drop 63.2% of the intensity. The range and rise refer to 63.2% of the total recovery intensity and time spent recovering.



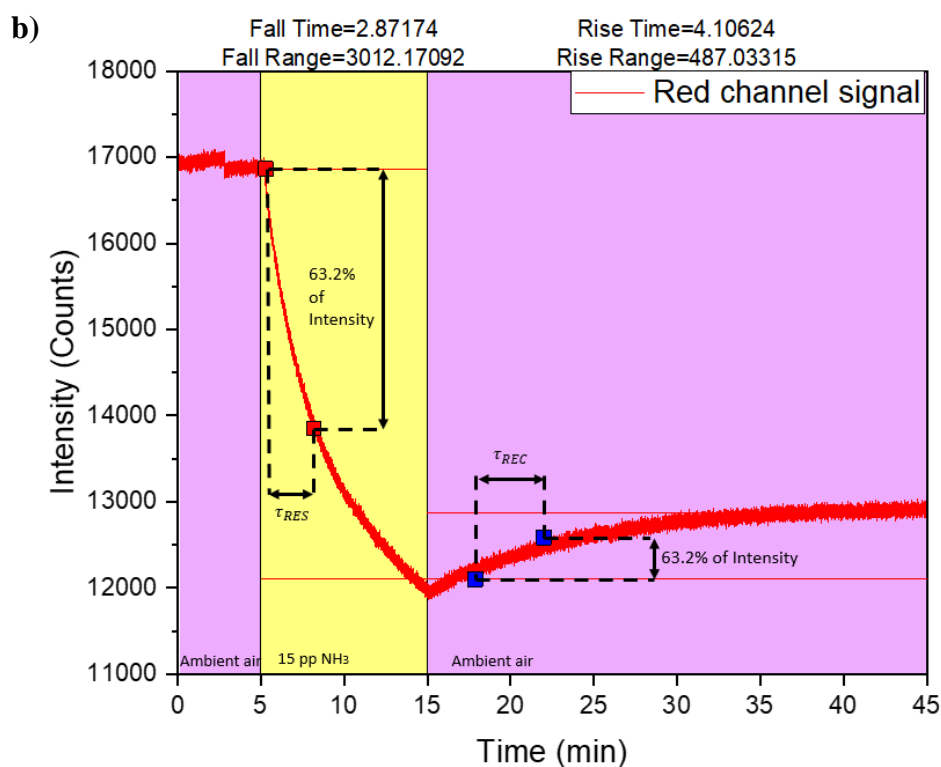


Figure 4.5: Signal Response of Paper-based sensor

As the paper-based sensor with different concentration of PVA respond to  $\text{NH}_3$  gas, the intensity would drop, giving different total intensity change, intensity fall range, and fall time (recorded in Table 4.2). The intensity of paper-based sensors increases back after the  $\text{NH}_3$  gas is turned off, and the total intensity change, intensity rise range, and rise time are recorded in Table 4.2. Among all the concentration, paper-based sensor with 50 mg/ml has the longest fall time and rise time when exposed to  $\text{NH}_3$  gas which is 3.07 minutes and 8.26 minutes respectively. This means that 50mg/ml required more time to change its colour intensity. On contrary, paper-based sensor with 0 mg/ml PVA has the shortest fall time ( $\tau_{RES} = 1.06$  minutes). Paper-based sensor with 20 mg/ml PVA has the shortest rise time among other concentration which is 4.11 minutes. This shows that the concentration of PVA has a significant effect on the colour change of paper-based sensor.



Table 4.2: Data obtained from transient response upon exposure  $\text{NH}_3$  gas.

<b>PVA Concentration</b>	<b><math>\Delta</math> Intensity</b>	<b>Intensity Fall Range</b>	<b>Fall Time, <math>\tau_{RES}</math> (min)</b>
<b>0mg/ml</b>	3124	1891.14	1.06
<b>10mg/ml</b>	4130	2567.36	1.83
<b>20mg/ml</b>	4857	3012.17	2.87
<b>30mg/ml</b>	3585	2232.17	2.38
<b>40mg/ml</b>	3126	1900.60	2.38
<b>50mg/ml</b>	3694	2276.59	3.07

Table 4.3: Data obtained from transient response during recovery.

<b>PVA Concentration</b>	<b><math>\Delta</math> Intensity</b>	<b>Intensity Rise Range</b>	<b>Rise Time, <math>\tau_{REC}</math> (min)</b>
<b>0mg/ml</b>	1980	1241.33	7.99
<b>10mg/ml</b>	1753	1047.20	7.50
<b>20mg/ml</b>	874	487.03	4.11
<b>30mg/ml</b>	1085	674.66	6.22
<b>40mg/ml</b>	697	381.10	4.37
<b>50mg/ml</b>	1164	694.26	8.26

## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusion

A colorimetric water-soluble gas sensor was successfully fabricated using red cabbage extract as the pH indicator and filter paper as the substrate. The colour change of the paper-based sensor is reddish-purple to pink when exposed to acidic gas and reddish-purple to green when exposed to alkaline gas, which indicates the paper-based sensor is able to detect water-soluble gas from pH 0 to 14. Among other concentrations of PVA, 20 mg/ml is the most suitable amount to use for a paper-based sensor. This is because, paper-based sensor with 20 mg/ml PVA has the highest total colour change when it is exposed to alkaline gas. The paper-based sensor with 30 mg/ml PVA has the highest total colour change upon exposure to acidic gas, but its peak shift is 0 nm. The total colour changes are large enough for the naked eye to detect. A colorimetric dye solution with 20 mg/ml PVA has the highest peak shift when exposed to both types of water-soluble gases. The colour changes captured using a smartphone show that a paper-based sensor with 20 mg/ml PVA has the strongest colour intensity observed by the naked eye. It is also shown that the total colour changes are related to the intensity observed by the naked eye, where a stronger intensity of the paper-based sensor would give a higher value of total colour changes. A paper-based sensor with 20 mg/ml PVA also has the fastest recovery time after exposure to ambient air. Thus, the paper-based sensor fabricated in this project is reversible, biodegradable, inexpensive, and non-zero-powered, which is useful for various applications that require rapid detection.

#### 5.2 Recommendations For Future Work

There are many parts of this work can be improved in the future for better understanding of the properties of the paper-based sensor and to obtain better results from it. In this project, the peak shift obtained by UV-Vis is 0 nm and the intensity of paper-based sensor was not obtainable by the optical reflective microchip when paper-based sensor was exposed HCl gas. This can be

improved by using other types of acidic gas such as sulfur dioxide or by increasing the amount HCl used to exposed in the gas chamber. Other than that, this work can be improved by adding temperature, humidity, and pressure sensor. This is because environmental changes of the project might affect the results obtained. It was mentioned by Hasanah and Imawan (2018), the storage condition and temperature has effect on the colour changes because oxidation reaction will occur on anthocyanin.

Extensions can be done to this project by including the study on maximum colour change achievable by the paper-based sensor. In this work, specific time was set for paper-based sensor to change its colour. However, the maximum colour changes achievable by the paper-based sensor, and the time taken to achieve it is unknown. This study is useful because the maximum colour achieved for recovery will be known and the reusability of this paper-based sensor can be determined. This improvement could also determine the relationship between exposure time and recovery time.

## REFERENCES

- Abedi-Firoozjah, R., Yousefi, S., Heydari, M., Seyedfatehi, F., Jafarzadeh, S., Mohammadi, R., Rouhi, M., & Garavand, F. (2022). Application of Red Cabbage Anthocyanins as pH-Sensitive Pigments in Smart Food Packaging and Sensors. *Polymers*, *14*(8), 1629. <https://doi.org/10.3390/polym14081629>
- Bogue, R. (2015). Detecting gases with light: a review of optical gas sensor technologies. *Sensor Review*, *35*(2), 133–140. <https://doi.org/10.1108/SR-09-2014-696>
- Brough, C., Miller, D. A., Keen, J. M., Kucera, S. A., Lubda, D., & Williams, R. O. (2016). Use of Polyvinyl Alcohol as a Solubility-Enhancing Polymer for Poorly Water-Soluble Drug Delivery (Part 1). *AAPS PharmSciTech*, *17*(1), 167–179. <https://doi.org/10.1208/s12249-015-0458-y>
- Chen, Y., Fu, G., Zilberman, Y., Ruan, W., Ameri, S. K., Zhang, Y. S., Miller, E., & Sonkusale, S. R. (2017). Low-cost smart phone diagnostics for food using paper-based colorimetric sensor arrays. *Food Control*, *82*, 227–232. <https://doi.org/10.1016/j.foodcont.2017.07.003>
- Chigurupati, N., Saiki, L., Gayser, C., & Dash, A. K. (2002). Evaluation of red cabbage dye as a potential natural color for pharmaceutical use. *International Journal of Pharmaceutics*, *241*(2), 293–299. [https://doi.org/10.1016/S0378-5173\(02\)00246-6](https://doi.org/10.1016/S0378-5173(02)00246-6)
- Deng, S., Doherty, W., McAuliffe, M. A., Salaj-Kosla, U., Lewis, L., & Huyet, G. (2016). A low-cost, portable optical sensing system with wireless communication compatible of real-time and remote detection of dissolved ammonia. *Photonic Sensors*, *6*(2), 107–114. <https://doi.org/10.1007/s13320-016-0291-2>

Doshi, R., & Panditrao, A. (n.d.). Non-Invasive Optical Sensor for Hemoglobin Determination. In *International Journal of Engineering Research and Applications (IJERA)* (Vol. 3). [www.ijera.com](http://www.ijera.com)

Gilchrist, A., & Nobbs, J. (2017). Colorimetry, Theory. In *Encyclopedia of Spectroscopy and Spectrometry* (pp. 328–333). Elsevier. <https://doi.org/10.1016/B978-0-12-803224-4.00124-2>

Hanafi, R., Mayasari, R. D., Masmui, Agustanhakri, Raharjo, J., & Nuryadi, R. (2019). *Electrochemical sensor for environmental monitoring system: A review*. 030007. <https://doi.org/10.1063/1.5132657>

Harpaz, D., Axelrod, T., Yitian, A., Eltzov, E., Marks, R., & Tok, A. (2019). Dissolvable Polyvinyl-Alcohol Film, a Time-Barrier to Modulate Sample Flow in a 3D-Printed Holder for Capillary Flow Paper Diagnostics. *Materials*, *12*(3), 343. <https://doi.org/10.3390/ma12030343>

Hasanah, B. H., & Imawan, C. (2018). Effect of Paper Matrix on the Properties of the Ammonia Gas Indicator Label. *Journal of Physics: Conference Series*, *1120*, 012032. <https://doi.org/10.1088/1742-6596/1120/1/012032>

Hsieh, Y. L. (2007). Chemical structure and properties of cotton. In *Cotton* (pp. 3–34). Elsevier. <https://doi.org/10.1533/9781845692483.1.3>

Jain, N., Singh, V. K., & Chauhan, S. (2017). A review on mechanical and water absorption properties of polyvinyl alcohol based composites/films. *Journal of the Mechanical Behavior of Materials*, *26*(5–6), 213–222. <https://doi.org/10.1515/jmbm-2017-0027>

Jamil, N., Husin, H., Alfida, A. W., Aman, Z., & Hassan, Z. (2018). Characterization and Preparation of Polyvinyl Alcohol (PVA) as Inhibitor in Formation of Hydrates. *International Journal of Current Research in Science*,

*Engineering & Technology*, 1(Spl-1), 578.  
<https://doi.org/10.30967/ijcrset.1.S1.2018.578-584>

Kan, V., Vargo, E., Machover, N., Ishii, H., Pan, S., Chen, W., & Kakehi, Y. (2017). Organic Primitives. *Proceedings of the 2017 CHI Conference on Human Factors in Computing Systems*, 989–1000.  
<https://doi.org/10.1145/3025453.3025952>

Kuswandi, B., Asih, N. P. N., Pratoko, D. K., Kristiningrum, N., & Moradi, M. (2020). Edible pH sensor based on immobilized red cabbage anthocyanins into bacterial cellulose membrane for intelligent food packaging. *Packaging Technology and Science*, 33(8), 321–332. <https://doi.org/10.1002/pts.2507>

Kwak, D., Lei, Y., & Maric, R. (2019). Ammonia gas sensors: A comprehensive review. *Talanta*, 204, 713–730.  
<https://doi.org/10.1016/j.talanta.2019.06.034>

Liana, D. D., Raguse, B., Gooding, J. J., & Chow, E. (2012). Recent Advances in Paper-Based Sensors. *Sensors*, 12(9), 11505–11526.  
<https://doi.org/10.3390/s120911505>

López-Marzo, A. M., & Merkoçi, A. (2016). Paper-based sensors and assays: a success of the engineering design and the convergence of knowledge areas. *Lab on a Chip*, 16(17), 3150–3176. <https://doi.org/10.1039/C6LC00737F>

Malins, C., Doyle, A., MacCraith, B. D., Kvasnik, F., Landl, M., Šimon, P., Kalvoda, L., Lukaš, R., Pufler, K., & Babusík, I. (1999). Personal ammonia sensor for industrial environments. *Journal of Environmental Monitoring*, 1(5), 417–422. <https://doi.org/10.1039/a904846d>

Nery, E. W., & Kubota, L. T. (2013). Sensing approaches on paper-based devices: a review. *Analytical and Bioanalytical Chemistry*, 405(24), 7573–7595. <https://doi.org/10.1007/s00216-013-6911-4>

Nie, Z., Deiss, F., Liu, X., Akbulut, O., & Whitesides, G. M. (2010). Integration of paper-based microfluidic devices with commercial electrochemical readers. *Lab on a Chip*, *10*(22), 3163. <https://doi.org/10.1039/c0lc00237b>

Nie, Z., Nijhuis, C. A., Gong, J., Chen, X., Kumachev, A., Martinez, A. W., Narovlyansky, M., & Whitesides, G. M. (2010). Electrochemical sensing in paper-based microfluidic devices. *Lab Chip*, *10*(4), 477–483. <https://doi.org/10.1039/B917150A>

Patari, S., & Mahapatra, P. S. (2020). Liquid Wicking in a Paper Strip: An Experimental and Numerical Study. *ACS Omega*, *5*(36), 22931–22939. <https://doi.org/10.1021/acsomega.0c02407>

Pinheiro, T., Cardoso, A. R., Sousa, C. E. A., Marques, A. C., Tavares, A. P. M., Matos, A. M., Cruz, M. T., Moreira, F. T. C., Martins, R., Fortunato, E., & Sales, M. G. F. (2021). Paper-Based Biosensors for COVID-19: A Review of Innovative Tools for Controlling the Pandemic. *ACS Omega*, *6*(44), 29268–29290. <https://doi.org/10.1021/acsomega.1c04012>

Popa, D., & Udrea, F. (2019). Towards Integrated Mid-Infrared Gas Sensors. *Sensors*, *19*(9), 2076. <https://doi.org/10.3390/s19092076>

Nisha, K. S., (2020). *Polyvinyl alcohol/beetroot dye film as light absorbing material in solar cell*. 020023. <https://doi.org/10.1063/5.0029894>

Sahu, P., & Gupta, M. (2022). Water absorption behavior of cellulosic fibres polymer composites: A review on its effects and remedies. *Journal of Industrial Textiles*, *51*(5\_suppl), 7480S-7512S. <https://doi.org/10.1177/1528083720974424>

Shen, L., Hagen, J. A., & Papautsky, I. (2012). Point-of-care colorimetric detection with a smartphone. *Lab on a Chip*, *12*(21), 4240. <https://doi.org/10.1039/c2lc40741h>

Shetti, N. P., Nayak, D. S., Reddy, K. R., & Aminabhvi, T. M. (2019). Graphene–Clay-Based Hybrid Nanostructures for Electrochemical Sensors and Biosensors. In *Graphene-Based Electrochemical Sensors for Biomolecules* (pp. 235–274). Elsevier. <https://doi.org/10.1016/B978-0-12-815394-9.00010-8>

Singh, A., Lantigua, D., Meka, A., Taing, S., Pandher, M., & Camci-Unal, G. (2018). Paper-Based Sensors: Emerging Themes and Applications. *Sensors*, *18*(9), 2838. <https://doi.org/10.3390/s18092838>

Yao, Z., Coatsworth, P., Shi, X., Zhi, J., Hu, L., Yan, R., Güder, F., & Yu, H.-D. (2022). Paper-based sensors for diagnostics, human activity monitoring, food safety and environmental detection. *Sensors & Diagnostics*, *1*(3), 312–342. <https://doi.org/10.1039/D2SD00017B>

Yeh, P., Yeh, N., Lee, C.-H., & Ding, T.-J. (2017). Applications of LEDs in optical sensors and chemical sensing device for detection of biochemicals, heavy metals, and environmental nutrients. *Renewable and Sustainable Energy Reviews*, *75*, 461–468. <https://doi.org/10.1016/j.rser.2016.11.011>